NASA CONTRACTOR REPORT

NASA CR-353

NASA CR-353

ANALYSES OF VAPORIZATION IN LIQUID URANIUM BEARING SYSTEMS AT VERY HIGH TEMPERATURES

by L. Kaufman and E. T. Peters

Prepared under Contract No. NAS 3
MANLABS, INC.
Cambridge, Mass.
for Lewis Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION · WASHINGTON, D. C. · DECEMBER 1965

NASA CR-353

ANALYSES OF VAPORIZATION IN LIQUID URANIUM BEARING SYSTEMS AT VERY HIGH TEMPERATURES

By L. Kaufman and E. T. Peters

Prepared under Contract No. NAS 3-7168 by
MANLABS, INC.
Cambridge, Mass.

for Lewis Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

FOREWORD

Research related to advanced nuclear rocket propulsion is described herein. This work was performed under NASA Contract Number NAS 3-7168 with Mr. Maynard F. Taylor, Nuclear Reactor Division, NASA Lewis Research Center as Technical Manager.

TABLE OF CONTENTS

		Page
1.	INTRODUCTION	1
2.	THERMODYNAMIC FORMULATION	3
3.	ANALYSIS OF SELECTED SYSTEMS	5
	a. Zr-C-U	8
	b. Nb-C-U	15
4.	POTENTIAL OF OTHER SYSTEMS	23
	References	24
	APPENDIX A - VAPOR PRESSURE DATA FOR CARBON POLYMORPHS	

1. INTRODUCTION

An analysis has been carried out to explore the feasibility of selecting a liquid uranium bearing material system which might function as a heat exchanger for hydrogen gas at 100 atm. pressure and 8,000 - 10,000° R. Additional constraints are imposed by the requirements of a high impulse nuclear engine.

The over-all objectives of this study are the identification of candidate elemental components to be alloyed with uranium, the specification of compositions which could provide possibilities for unique stability such as congruencies, and the comparison of mass loss rates due to vaporization of elemental components from the liquid surface and diffusion of backing material into the liquid. end

The investigation carried out has concerned a reference ternary system U-X_1-X_2 having the following characteristics:

a) The system, when heated to temperatures between 8,000 - 10,000° R in contact with 100 atm. of hydrogen gas, will exhibit a partial pressure of uranium less than or equal to 0.016 atm.

b) None of the components considered for inclusion (i.e., X_1 and X_2) shall have a nuclear capture cross section greater than 5 barns.

c) The selection of X_1 and X_2 will be subject to the requirement that the average molecular weight of $U + X_1 + X_2$ plus hydrogen at temperatures between 8,000° R and 10,000° R shall not exceed that of pure hydrogen by a factor which is more than 1.5.

d) The atomic fraction of uranium in the alloy will be constrained to lie between 0.001 and 0.02.

Based upon the initial choice of components (X_1 = Zr or Nb and X_2 = C) the existence or nonexistence of congruency potential in the U-X_1-X_2 system has been investigated by assuming that the liquid can be approximated by a regular solution.

2. THERMODYNAMIC FORMULATION

The free energy of the liquid phase of a ternary system X_1-X_2-U is given by:

$$F^L = (1-x-y)\,F^L_{X_1} + x\,F^L_{X_2} + y\,F^L_U + F^L_E + RT\Big((1-x-y)\ln(1-x-y) + x\ln x + y\ln y\Big) \qquad (1)$$

where x = atomic fraction of element X_2 and y = atomic fraction of uranium, and F^L_E, the excess free energy of mixing, is given by

$$F^L_E = (1-x-y)\,x\,L_{X_1-X_2} + x\,y\,L_{X_2-U} + (1-x-y)\,y\,L_{X_1-U} \qquad (2)$$

where the L terms are constants (1*).

The partial molar free energies of each component are, by definition**

$$\bar{F}^L_{X_1} = F^L - x\left(\frac{\partial F^L}{\partial x}\right)_y - y\left(\frac{\partial F^L}{\partial y}\right)_x \qquad (3a)$$

$$\bar{F}^L_{X_2} = F^L + (1-x)\left(\frac{\partial F^L}{\partial x}\right)_y - y\left(\frac{\partial F^L}{\partial y}\right)_x \qquad (3b)$$

$$\bar{F}^L_U = F^L - x\left(\frac{\partial F^L}{\partial x}\right)_y + (1-y)\left(\frac{\partial F^L}{\partial y}\right)_x \qquad (3c)$$

Differentiation and combination with Eq. (1) yields

$$\bar{F}^L_{X_1} = F^L_{X_1} + RT\ln(1-x-y) + \bar{F}^L_{E-X_1} \qquad (4a)$$

$$\bar{F}^L_{X_2} = F^L_{X_2} + RT\ln x + \bar{F}^L_{E-X_2} \qquad (4b)$$

---

* Underscored numbers in parentheses designate References given at end of report.

** The partial molar excess free energies, i.e., $\bar{F}^L_{E-X_1}$ etc., are defined in the same manner.

$$\overline{F}_{U}^{L} = F_{U}^{L} + RT \ln y + \overline{F}_{E-U}^{L} \tag{4c}$$

The approximations that have been indicated above and Eqs. (1) and (3) give

$$\overline{F}_{E-X_1}^{L} = L_{X_1-X_2}(x^2 + xy) - L_{X_2-U}(xy) + L_{X_1-U}(y^2 + xy) \tag{5a}$$

$$\overline{F}_{E-X_2}^{L} = L_{X_1-X_2}((1+x)^2 - y(1-x) + L_{X_2-U}\, y(1-x) - L_{X_1-U}\, y(1-x-y) \tag{5b}$$

$$\overline{F}_{E-U}^{L} = -L_{X_1-X_2}\, x(1-x-y) + L_{X_2-U}\, x(1-y) + L_{X_1-U}((1-y)^2 - x(1-y)) \tag{5c}$$

Since $\overline{F}_i^L - F_i^o \equiv RT \ln a_i^L / a_i^o = RT \ln p_i / p_i^o$, where i stands for any component, Eqs. (1)-(5) yields

$$\log (p_{X_1}/p_{X_1}^o) = \log(1-x-y) + (1/4.575T)\, \overline{F}_{E-X_1}^{L} \tag{6a}$$

$$\log (p_{X_2}/p_{X_2}^o) = \log x + (1/4.575T)\, \overline{F}_{E-X_2}^{L} \tag{6b}$$

$$\log (p_U/p_U^o) = \log y + (1/4.575T)\, \overline{F}_{E-U}^{L} \tag{6c}$$

where the excess free energies are given by Eq. (5), temperature is in degrees Kelvin and the logs refer to base ten.

Eq. (6) completely specifies the equilibrium partial pressures of X_1, X_2, and U as a function of composition. The average molecular weight ($\tilde{M}$) of the gaseous phase is given by

$$\tilde{M} = \frac{\Sigma M_i p_i}{P_T} \tag{7}$$

where the total pressure $P_T = \Sigma p_i$.

3. ANALYSIS OF SELECTED SYSTEMS

The desirable characteristics for selecting X_1 and X_2 are low atomic weight, refractoriness, i.e., low vapor pressure at high temperature, low activity of both species in X_1-X_2 alloys, and low nuclear capture cross sections (see Table 1). The elements which most nearly fulfill these conditions are X_1 = Nb or Zr and X_2 = C. The L factors required for Eq. (5) are calculated by appropriate equilibration of the free energy of liquid (L) and solid (σ) at a composition of 0.5 (2). For the Zr-C case,

$$L_{Zr-C} = 4(\Delta F^{\sigma}[\overline{T}^{\sigma}] + \overline{T}^{\sigma} R \ln 2 + 0.5 \Delta F^{L \rightarrow \gamma}[\overline{T}^{\sigma}])$$

This yields

$$L_{Zr-C} = -36{,}080 \text{ cal/mol.} \tag{8a}$$

Similarly

$$L_{Nb-C} = -37{,}500 \text{ cal/mol.} \tag{8b}$$

$$L_{U-C} = -36{,}000 \text{ cal/mol. } (3) \tag{8c}$$

The β phase of the Nb-U system (4) exhibits a miscibility gap at $1300^{\circ}K = T_C$; the β/L equilibria decreases linearly from $\overline{T}^{\beta}_{Nb}$ to $\overline{T}^{\beta}_{U}$. Hence,

$$L_{Nb-U} \approx 2RT_C \approx +5{,}200 \text{ cal/mol.} \tag{8d}$$

TABLE 1

NUCLEAR CAPTURE CROSS SECTIONS, σ (barns) (5)

Element	σ	Element	σ
C	0.004	Nb	1.1
B^{11}	0.05	Ta	21.3
N	1.9	Cr	2.9
O	0.0002	Mo	2.5
Si	0.13	W^{184}	2.0 → 5.0
Ti	5.6	$W^{Natural}$	19.2
Zr	0.18	U^{235}	6.00
Hf	105	$U^{Natural}$	7.5
V	5.0		

According to the initial conditions, the atomic fraction of uranium is constrained to lie between 0.001 and 0.02, i.e., $y_{max} = 0.02$. The y terms in Eqs. (5a) and (5b) become very small and can be ignored. The equilibrium partial pressures for the Nb-C-U ternary system are therefore given as

$$\log (p_{Nb}/p^{o}_{Nb}) \approx \log (1-x) - 37,500\, x^2/4.575\, T \quad (9a)$$

$$\log a_C \approx \log x - 37,500\, (1-x)^2/4.575\, T \; ^{*} \quad (9b)$$

$$\log (p_U/p^{o}_U) = \log y + (1/4.575\, T)(-37,500\, x^2 - 3700\, x(1-y) + 5200\, (1-y)^2) \quad (9c)$$

and, assuming $L_{Nb-U} \approx L_{Zr-U}$, the equilibrium partial pressures for the Zr-C-U ternary system are

$$\log (p_{Zr}/p^{o}_{Zr}) \approx \log (1-x) - 36,080\, x^2/4.575\, T \quad (10a)$$

$$\log a_C \approx \log x - 36,080\, (1-x)^2/4.575\, T \quad (10b)$$

$$\log (p_U/p^{o}_U) = \log y + (1/4.575\, T)(-36,080\, x^2 - 5120\, x(1-y) + 5200(1-y)^2) \quad (10c)$$

---

* The total partial pressure of carbon (p_C (total)) is taken as the vapor pressure of the monomer C plus the pressures of the polymers C_2, C_3, C_4, and C_5. For the general reaction $nC\,(s) \rightleftarrows C_n(v)$, one determines the partial pressure of the n polymer from the expression

$$p_{C_n} = a_C^n\, p^{o}_{C_n}$$

The pressures of the polymers over pure carbon and the tabulations of p_C (total) required for the various systems studied are presented in Appendix A.

Values of $\log p^{o}$ vs. T for the various elements of concern are tabulated in Table 2. When necessary, the data were extrapolated to $10,000^{o}$ R ($\sim 5555^{o}$ K) by means of the formula

$$\log p^{o} = a/T\,^{o}K + b \tag{11}$$

with the constants a and b being evaluated from the high temperature data.

a) <u>Zr-C-U</u>

The partial pressures of Zr and C were calculated as a function of x at 9000^{o} R according to Eqs. (10a) and (10b). The calculation steps are tabulated in Table 3 and the results are presented in Figure 1. The pressures of Zr plus C are a minimum at x = 0.30. This value is used in Eq. (10c) for calculation of P_U as a function of y between the imposed limits of 0.001 and 0.02. These calculations are tabulated in Table 4a. With reference to Eq. (10a), it is seen that $\bar{F}^{L}_{E-U}$ term becomes more negative as x increases. Therefore, high C content reduces the vapor pressure of U, y held constant.

The average molecular weight of the gaseous mixture ($\tilde{M}$) is calculated as a function of x by means of Eq. (7) for $T=9000^{o}$ R, $p^{o}_{U} = 4.677$, and $P_H = 100$ atm at y = 0.001, 0.01, and 0.02. (The molecular weight of hydrogen vs. temperature at 100 atm. is plotted in Figure 2.) The results are tabulated in Table 4b and are presented graphically in Figure 3. The condition that the average molecular weight of the gaseous mixture be no more than 1.5 times the molecular weight of hydrogen is not met by the Zr-C-U-H system at 9000^{o} R.

TABLE 2

THE VAPOR PRESSURES OF U, Zr, AND Nb

AS A FUNCTION OF TEMPERATURE

T(°K)	T(°R)	$\log p_U{}^o$(6)	$\log p_U{}^o$(7)	$\log p_U{}^o$(8)	$\log p_{Zr}{}^o$(9)	$\log p_{Nb}{}^o$(10)
3000	5,400	-2.11	-2.08	-2.79	-3.66	-4.78
3200	5,760	-1.63	-1.60	-2.25	-3.03	-4.40
3400	6,120	-1.20	-1.17	-1.77	-2.49	-3.39
3600	6,480	-0.82	-0.79	-1.35	-2.02	-2.81
3800	6,840	-0.48	-0.44	-0.97	-1.56	-2.29
4000	7,200	-0.18	-0.14	-0.63	-1.17	-1.82
4100	7,380	-0.03	0.01	-0.47	-0.99	-1.61
4200	7,560		0.14	-0.32	-0.82	-1.40
4300	7,740		0.27	-0.17	-0.65	-1.20
4400	7,920		0.39	-0.04	-0.49	-1.02
4500	8,100		0.51	+0.09	-0.35	-0.84
4600	8,280		0.63	0.22	-0.20	-0.67
4700	8,460		0.73	0.34	-0.06	-0.50
4800	8,640		0.84	0.45	0.07*	-0.34
4900	8,820		0.94	0.57	0.19*	-0.19
5000	9,000		1.03	0.67	0.31*	-0.05
5100	9,180		1.12	0.77		0.09*
5200	9,360		1.21	0.87		0.22*
5300	9,540		1.30	0.96		0.34*
5400	9,720		1.38	1.14		0.47*
5500	9,900		1.46	1.23		0.58*
5555	10,000		1.50	1.27		0.65*
5600	10,080		1.53	1.31		0.70*

* Extrapolated

TABLE 3

CALCULATION PARAMETERS FOR THE PARTIAL PRESSURES OF ZIRCONIUM AND CARBON OVER Zr-C ALLOYS AT 9000°R

x	x^2	(1-x)	log(1-x)	$\log(p_{Zr}/p_{Zr}^{o})$	(p_{Zr}/p_{Zr}^{o})	p_{Zr}
0.01	10^{-4}	0.99	-0.0044	-0.0045	0.9897	2.021
0.10	0.01	0.90	-0.0458	-0.0592	0.8726	1.782
0.20	0.04	0.80	-0.0969	-0.1505	0.7071	1.444
0.30	0.09	0.70	-0.1549	-0.2755	0.5303	1.083
0.40	0.16	0.60	-0.2219	-0.4363	0.3662	0.748
0.50	0.25	0.50	-0.3010	-0.6360	0.2312	0.472
0.60	0.36	0.40	-0.3979	-0.8803	0.1317	0.269
0.70	0.49	0.30	-0.5229	-1.1795	0.0662	0.135
0.80	0.64	0.20	-0.6990	-1.5566	0.0278	0.0569
0.90	0.81	0.10	-1.0000	-2.0854	0.0082	0.0168
0.99	0.98	0.01	-2.0000	-3.3132	0.0005	0.0010

(1-x)	$(1-x)^2$	x	log x	$\log(a_C)$	a_C	p_C (Total)
0.99	0.98	0.01	-2.00	-3.3132	0.0005	0.0023
0.90	0.81	0.10	-1.00	-2.0854	0.0082	0.0384
0.80	0.64	0.20	-0.699	-1.5566	0.0278	0.140
0.70	0.49	0.30	-0.5229	-1.1795	0.0662	0.380
0.60	0.36	0.40	-0.3979	-0.8803	0.1317	0.896
0.50	0.25	0.50	-0.3010	-0.6360	0.2312	2.08
0.40	0.16	0.60	-0.2219	-0.4363	0.3662	4.76
0.30	0.09	0.70	-0.1549	-0.2755	0.5303	10.33
0.20	0.04	0.80	-0.0969	-0.1505	0.7071	20.48
0.10	0.01	0.90	-0.0458	-0.0592	0.8726	35.33
0.01	10^{-4}	0.99	-0.0044	-0.0045	0.9897	50.00

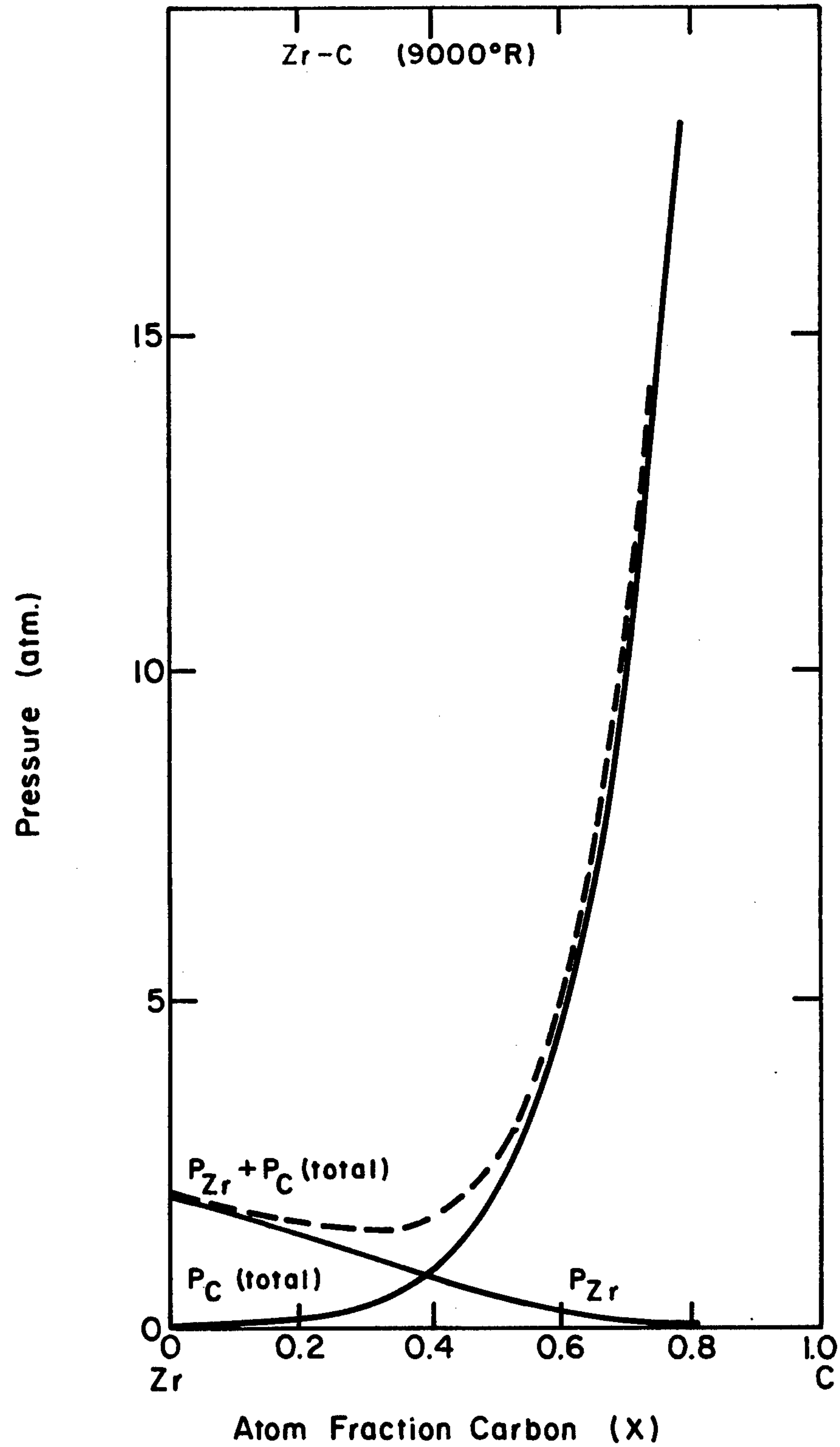

Figure 1. The Partial Pressures of Zirconium and Carbon at 9000° R as a Function of Alloy Composition.

TABLE 4

THE PARTIAL PRESSURE OF URANIUM OVER
Zr-C-U ALLOYS AT 9000°R

a) x = 0.30

y	log y	$\bar{F}^{L}_{E-U}$	$\log(p_U/p_U^o)$	$(p_U/p_U^o) \times 10^2$	p_U (7)	p_U (8)
0.001	-3.0	+0.018	-2.982	0.104	0.0112	0.0049
0.005	-2.301	+0.016	-2.285	0.412	0.0442	0.0192
0.010	-2.0	+0.014	-1.986	1.033	0.1107	0.0483
0.015	-1.824	+0.012	-1.812	1.542	0.1653	0.0721
0.020	-1.699	+0.010	-1.689	2.047	0.2194	0.0958

b) $y = 0.001$; $p_U^o = 4.678$ (8)

x	$\bar{F}^{L}_{E-U}$	$\log(p_U/p_U^o)$	$(p_U/p_U^o) \times 10^3$	p_U (8)	$\tilde{M}$	$\tilde{M}$ (y = 0.01)	$\tilde{M}$ (y = 0.02)
0.10	+0.194	-2.806	1.563	.0073	3.125	3.273	3.435
0.20	+0.131	-2.869	1.352	.0063	2.840	2.968	3.109
0.30	+0.036	-2.964	1.086	.0051	2.551	2.654	2.767
0.40	-0.099	-3.099	0.796	.0037	2.336	2.412	2.494
0.50	-0.249	-3.249	0.564	.0026	2.322	2.375	2.433
0.60	-0.438	-3.438	0.365	.0017	2.747	2.768	2.817

$1.5 \times M_H = 2.303$

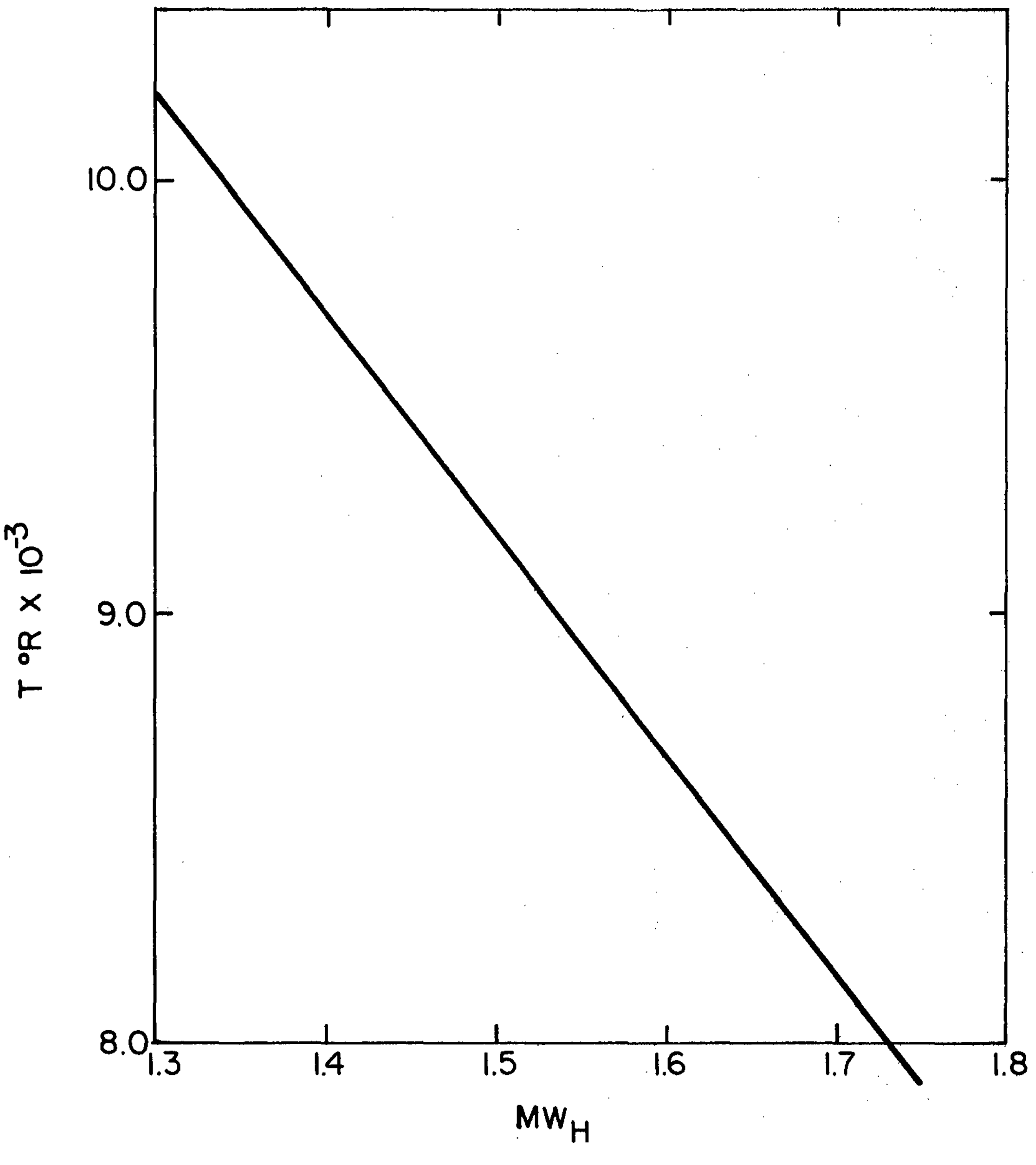

Figure 2. Molecular Weight of Hydrogen as a Function of Temperature (5) (Pressure = 100 atm.).

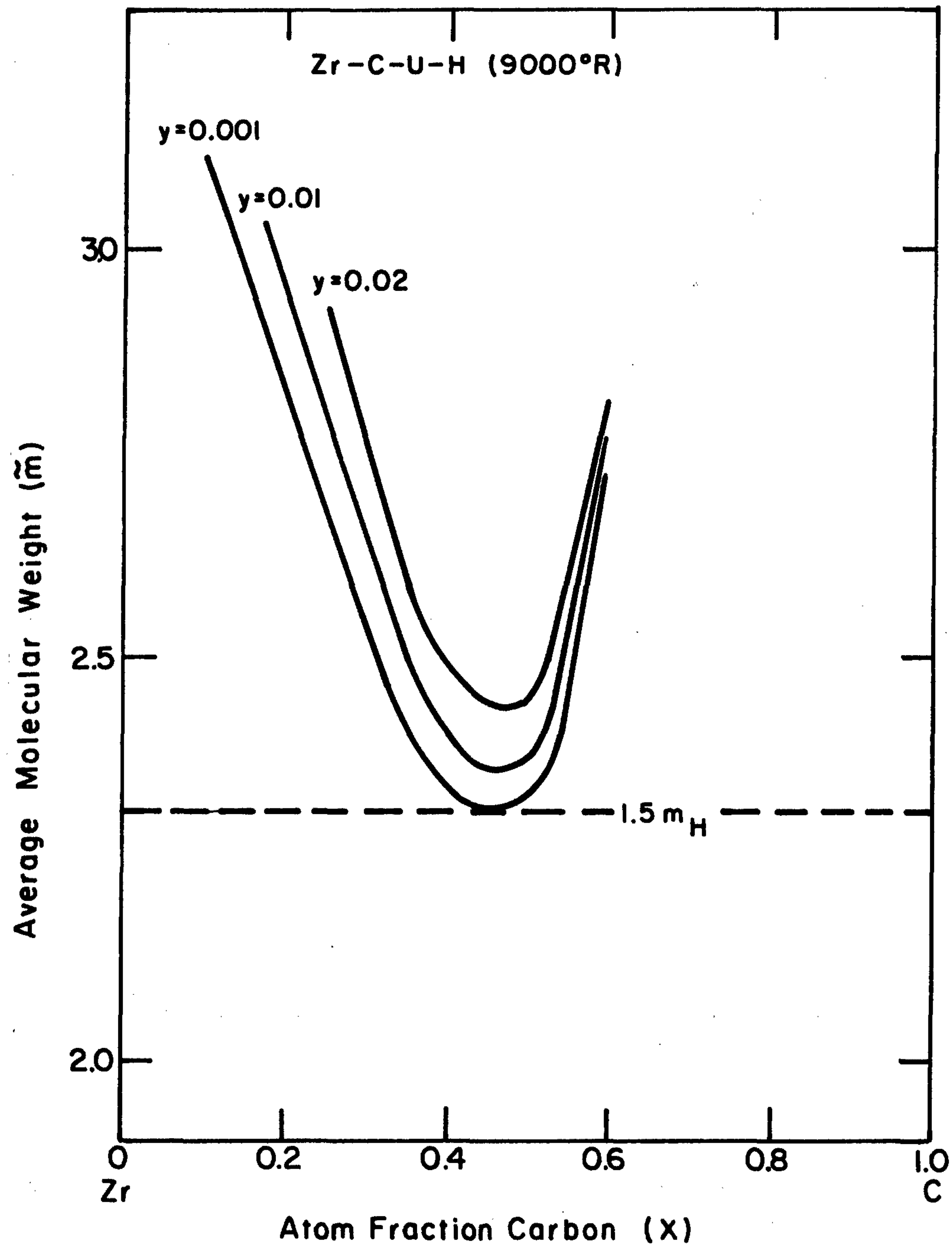

Figure 3. Average Molecular Weight of Gaseous Zr-C-U-H at 9000° R for Variable Zr-C Compositions.

b) Nb-C-U

The partial pressures of Nb and C were calculated as a function of x at 9000 and 10,000^{o} R according to Eqs. (9a) and (9b). The results are presented in Table 5 and Figures 4 and 5. The compositions at which Nb plus C is a minimum are x= 0.25 (9000^{o} R) and x= 0.23 (10,000^{o} R). These compositions were used together with Eq. (9c) to determine the partial pressure of uranium for y= 0.001 to y= 0.020 (Table 6a and 7a). The partial pressure of uranium (y= 0.001) and the average molecular weight of the gaseous mixture as a function of x (for y= 0.001, 0.01, and 0.02) are given in Tables 6b and 7b and are plotted in Figure 6 and 7. The average molecular weight of the gaseous mixture is less than 1.5 x MW_H over a selected range of x at 9000^{o} R but is greater than 1.5 x MW_H for all compositions at 10,000^{o} R.

TABLE 5

CALCULATION PARAMETERS FOR THE PARTIAL PRESSURES

NIOBIUM AND CARBON OVER

Nb-C ALLOYS AT 9000 AND 10,000° R

a) 9000° R

x	x^2	log(1-x)	$\log(p_{Nb}/p^{o}_{Nb})$	(p_{Nb}/p^{o}_{Nb})	p_{Nb}	p_C(Total)
0.01	10^{-4}	-0.0044	-0.0045	0.9897	0.8821	0.001
0.10	0.01	-0.0458	-0.0622	0.8470	0.7549	0.02
0.20	0.04	-0.0969	-0.1625	0.6880	0.6132	0.08
0.30	0.09	-0.1549	-0.3024	0.4984	0.4442	0.25
0.40	0.16	-0.2219	-0.4841	0.3280	0.2923	0.65
0.50	0.25	-0.3010	-0.7108	0.1964	0.1734	1.61
0.60	0.36	-0.3979	-0.9880	0.1028	0.0916	3.86
0.70	0.49	-0.5229	-1.3260	0.0472	0.0421	9.00
0.80	0.64	-0.6990	-1.7479	0.0179	0.0159	19.06
0.90	0.81	-1.0000	-2.3276	0.0047	0.0042	32.49
0.99	0.98	-2.0000	-3.6062	0.0003	0.0002	48.92

b) 10,000° R

x	$\log(p_{Nb}/p^{o}_{Nb})$	(p_{Nb}/p^{o}_{Nb})	p_{Nb}	p_C (Total)
0.01	-0.0045	0.9897	4.421	0.01
0.10	-0.0606	0.8698	3.885	0.16
0.20	-0.1559	0.6984	3.120	0.58
0.30	-0.2877	0.5168	2.309	1.52
0.40	-0.4581	0.3483	1.556	3.46
0.50	-0.6700	0.2138	0.955	7.48
0.60	-0.9293	0.1177	0.526	16.29
0.70	-1.2461	0.0567	0.253	36.10
0.80	-1.6436	0.0227	0.101	76.15
0.90	-2.1956	0.0064	0.028	142.87
0.99	-3.4465	0.0004	0.002	214.54

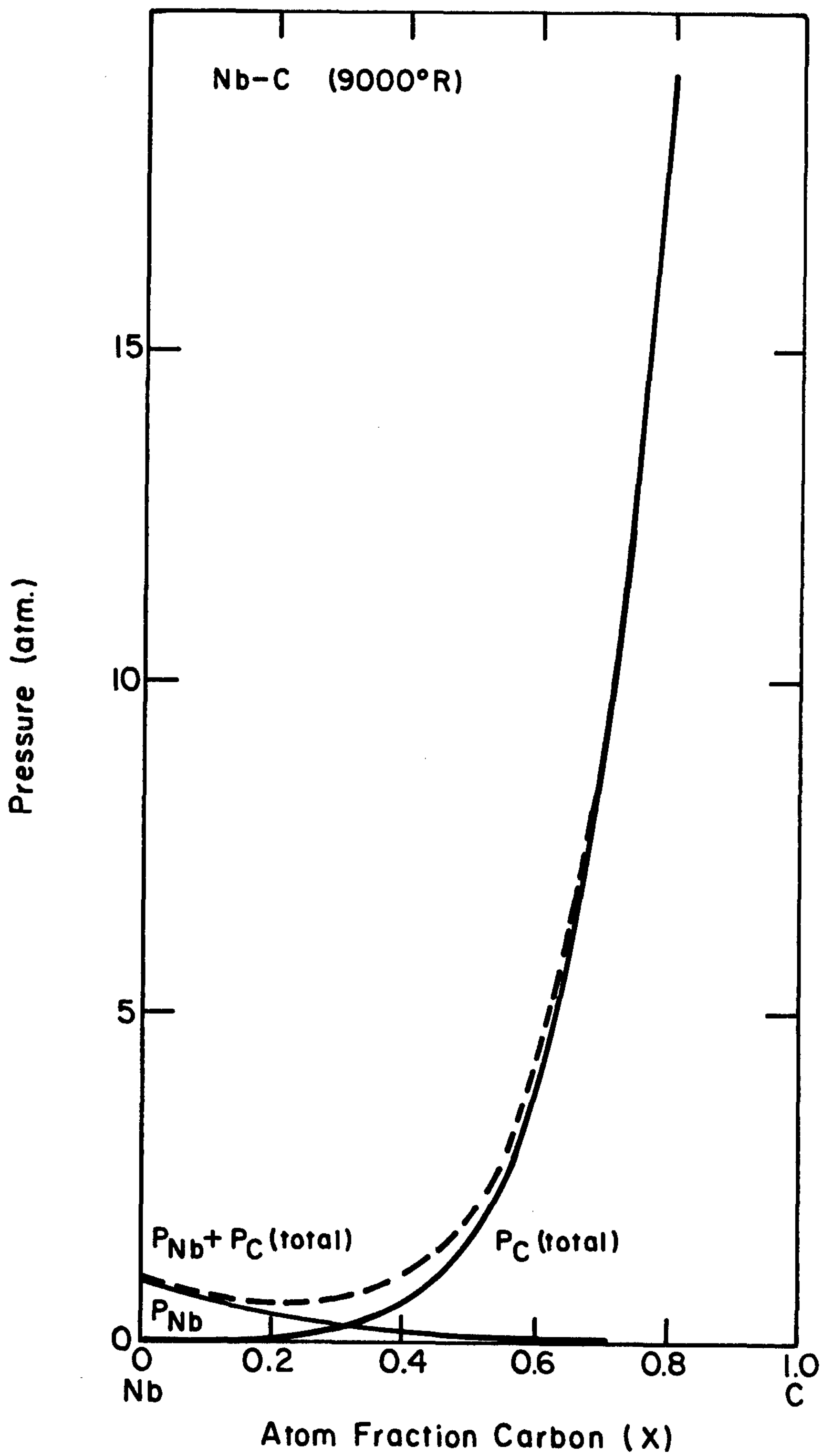

Figure 4. The Partial Pressures of Niobium and Carbon at 9000° R as a Function of Alloy Composition.

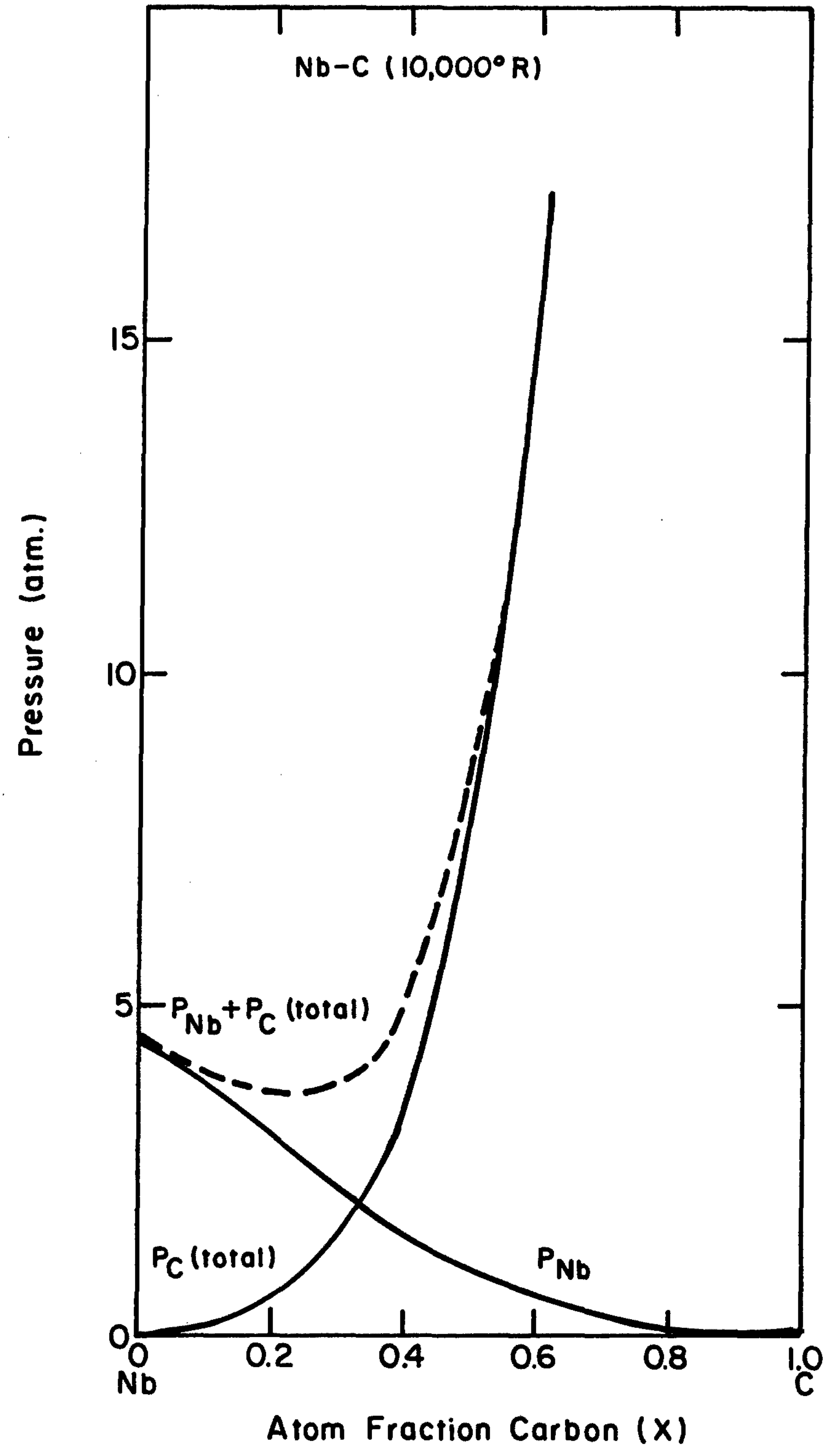

Figure 5. The Partial Pressures of Niobium and Carbon at 10,000^{o} R as a Function of Alloy Composition.

TABLE 6

THE PARTIAL PRESSURE OF URANIUM OVER

Nb-C-U ALLOYS AT 9000°R

a) $x = 0.25$

y	log y	$\overline{F}^{L}_{E-U}$	$\log(p_U/p^{o}_{U})$	$(p_U/p^{o}_{U}) \times 10^2$	p_U (7)	p_U (8)
0.001	-3.0	+0.084	-2.916	0.121	0.0130	0.0057
0.005	-2.301	+0.082	-2.219	0.604	0.0647	0.0283
0.010	-2.0	+0.080	-1.920	1.203	0.129	0.0563
0.015	-1.824	+0.078	-1.746	1.795	0.192	0.0840
0.020	-1.699	+0.076	-1.623	2.382	0.255	0.1114

b) $y = 0.001$, $p^{o}_{U} = 4.677$

x	$\overline{F}^{L}_{E-U}$	$\log(p_U/p^{o}_{U})$	$(p_U/p^{o}_{U}) \times 10^3$	p_U (8)	$\tilde{M}$	$\tilde{M}$ (y=0.01)	$\tilde{M}$ (y=0.02)
0.10	+0.194	-2.806	1.563	0.0073	2.239	2.389	2.650
0.20	+0.129	-2.871	1.346	0.0063	2.115	2.244	2.469
0.30	+0.031	-2.969	1.074	0.0050	1.984	2.087	2.264
0.40	-0.100	-3.100	0.794	0.0037	1.899	1.976	2.110
0.50	-0.264	-3.264	0.545	0.0025	1.969	2.021	2.111
0.60	-0.460	-3.460	0.347	0.0016	2.395	2.428	2.485

$1.5 \times M_H = 2.303$

TABLE 7

THE PARTIAL PRESSURE OF URANIUM OVER

Nb-C-U ALLOYS AT 10,000°R

a) x = 0.23

y	log y	$\bar{F}^{L}_{E-U}$	$\log(p_U/p^o_U)$	$(p_U/p^o_U) \times 10^2$	p_U (7)	p_U (8)
0.001	-3.0	+0.101	-2.899	0.126	0.0399	0.0235
0.005	-2.301	+0.099	-2.202	0.628	0.1990	0.1170
0.010	-2.0	+0.097	-1.913	1.250	0.395	0.233
0.015	-1.824	+0.096	-1.728	1.871	0.592	0.348
0.020	-1.699	+0.094	-1.605	2.483	0.785	0.462

b) y = 0.001, p^o_U = 18.62

x	$\bar{F}^{L}_{E-U}$	$\log(p_U/p^o_U)$	$(p_U/p^o_U) \times 10^3$	p_U (8)	$\tilde{M}$	$\tilde{M}$ (y = 0.01)	$\tilde{M}$ (y = 0.02)
0.10	+0.175	-2.825	1.496	0.0219	4.837	5.385	6.042
0.20	+0.116	-2.884	1.306	0.0243	4.210	4.691	5.269
0.30	+0.028	-2.972	1.067	0.0198	3.591	3.984	4.458
0.40	-0.090	-3.090	0.813	0.0151	3.158	3.456	3.813
0.50	-0.237	-3.237	0.593	0.0110	3.255	3.459	3.707
0.60	-0.414	-3.414	0.386	0.0072	4.589	4.715	4.867

$1.5 \times M_H = 2.01$

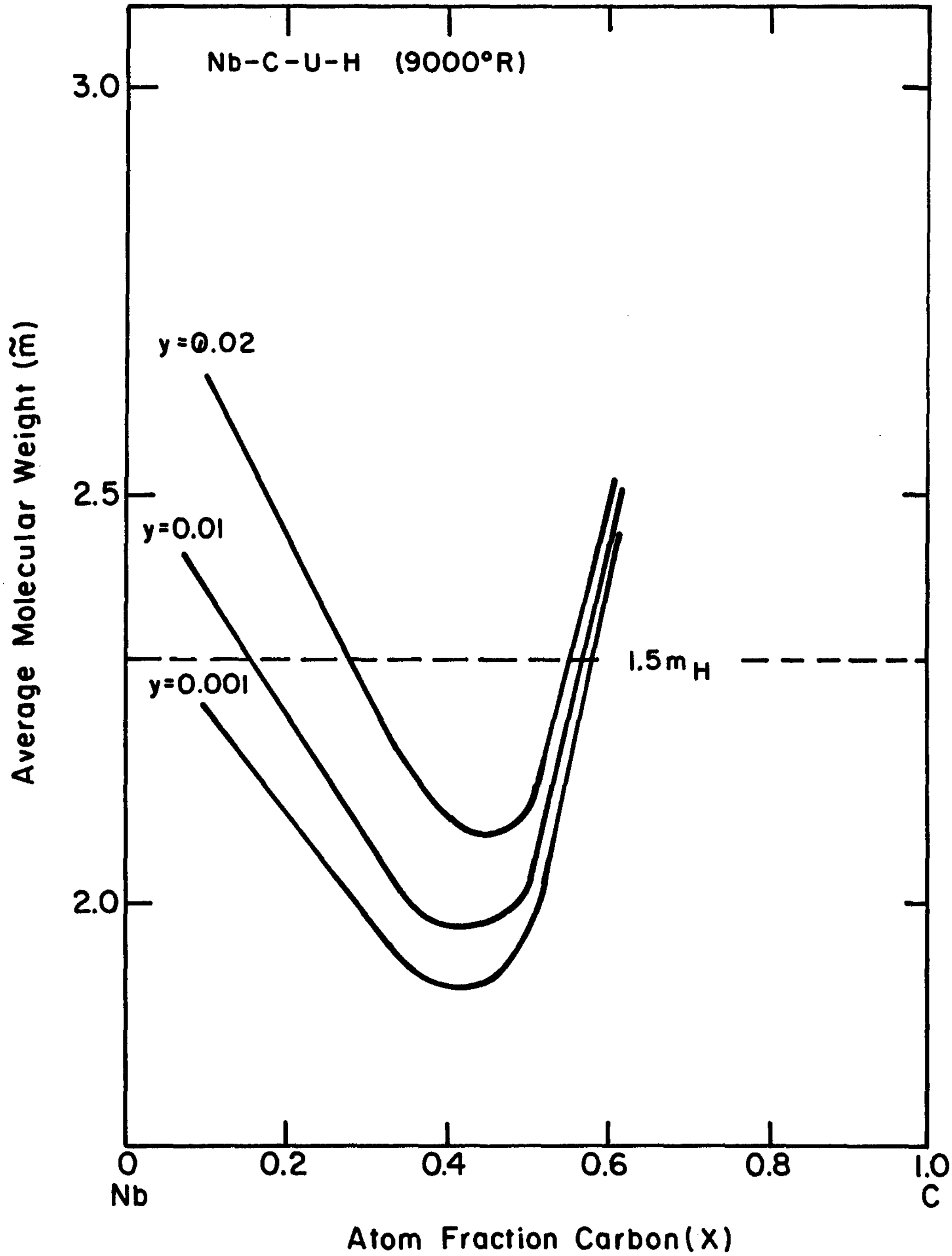

Figure 6. Average Molecular Weight of Gaseous Nb-C-U-H at 9000°R for Variable Nb-C Compositions.

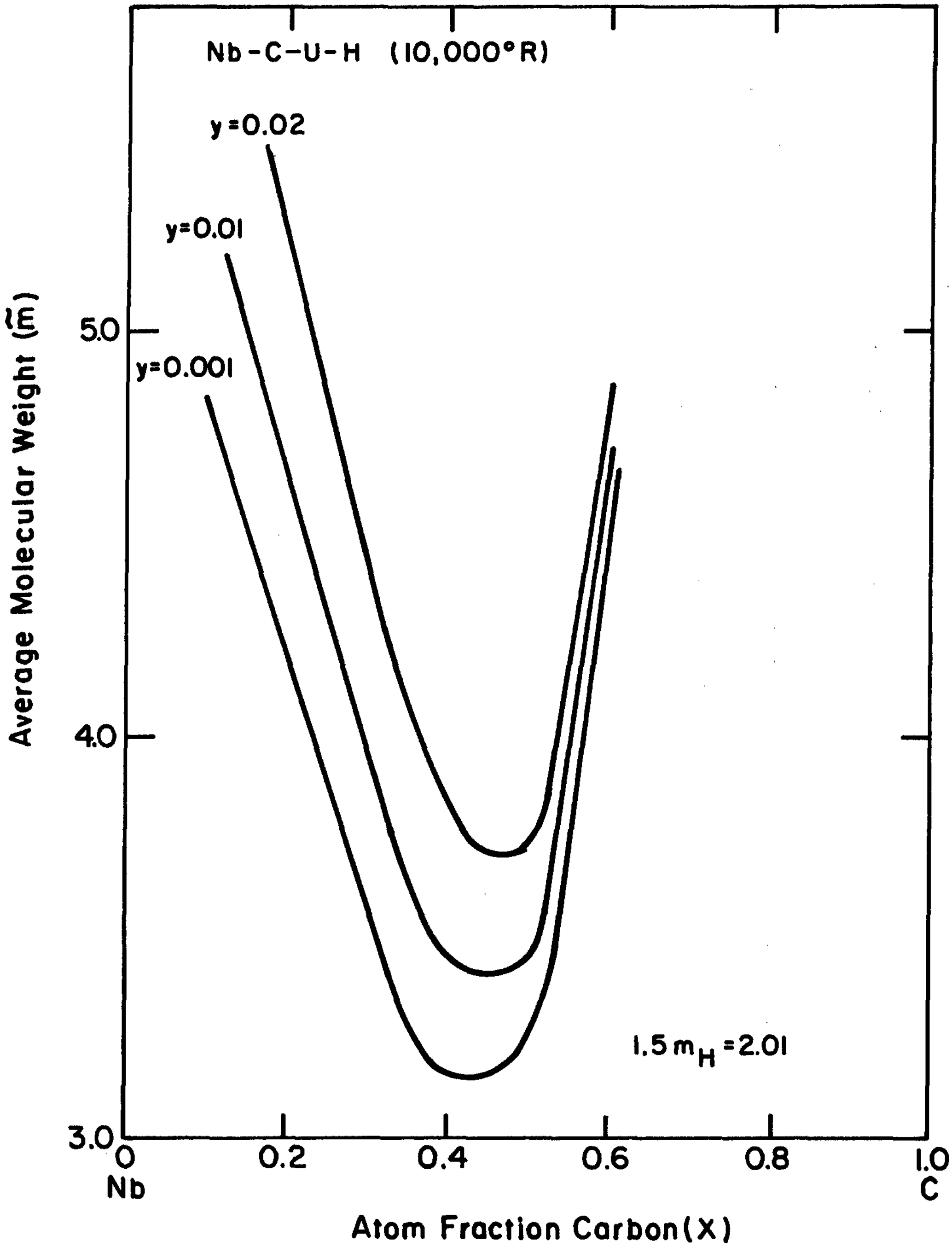

Figure 7. Average Molecular Weight of Gaseous Nb-C-U-H at 10,000° R for Variable Nb-C Compositions.

4. POTENTIAL OF OTHER SYSTEMS

Selection of other elements for X_1 and X_2 is generally precluded by one or more of the following unfavorable conditions:

1) High nuclear capture cross sections,
2) High vapor pressure over the element in the temperature range of interest, and
3) Unfavorable excess free energy of mixing.

The common refractory metals must be eliminated on the basis of condition 1), with the possible exceptions of molybdenum and tungsten 184 (see Table 1). The free energies of formation of Mo-C compounds are less negative than the Zr-C and Nb-C compounds, and the activity (and thus, partial pressure) of Mo in Mo-C alloys is higher over the practical range of alloy composition.

W^{184}-C-U alloys are expected to have properties similar to those studied. It is recommended that this system be considered for a future investigation.

Of the non-metals (X_2), boron is the most likely candidate. However, at 9000° R the vapor pressure of boron over pure boron is about ten times the vapor pressure of carbon over pure carbon. As the heats of formation of MeB and MeC compounds are comparable, there would not be a sufficient increase in the negativity of the excess free energy of mixing to offset the increased boron partial pressures.

It is considered to be most appropriate to re-evaluate the initial constraints listed in the introduction in light of the findings that are reported herein.

References

1. Kaufman, L. and Stepakoff, G., "Third Conference on Performance of High Temperature Systems" (Gorden and Breach Science Publishers, New York, 1965).

2. Kaufman, L. and Clougherty, E. V., "Metallurgy at High Pressures and High Temperatures" (Gorden and Breach Science Publishers, New York, 1964) p. 322.

3. The U-C and Pu-C Systems, Technical Report 14, International Atomic Energy Commission, Vienna, 1963.

4. Hansen, M. and Anderko, K., "Constitution of Binary Alloys", McGraw Hill Book Company, New York, 1958, p. 1021.

5. Private Communication with F. Rom, NASA, Cleveland, Ohio.

6. AVCO Report, Air Force Contract No. AF33(657)-8232, 15 June 1963.

7. Rauh, E. G. and Thorn, R. J., J. Chem. Phy., 22 (1954), 1414.

8. Maria, G. D., Burns, R. P., Drowart, J. and Inghram, M., J. Chem. Phy., 32 (1960) 1373.

9. JANAF Thermochemical Tables, Dow Chemical Company, Midland, Michigan, 30 June 1961.

10. AVCO Report, Air Force Contract No. AF33(657)-8232, 15 March 1963, p. 153.

11. JANAF Thermochemical Tables, Dow Chemical Company, Midland, Michigan.

APPENDIX A

VAPOR PRESSURE DATA FOR CARBON POLYMORPHS

TABLE 1A

VAPOR PRESSURE OF C_1, C_2, C_3, C_4 AND C_5 (11)

T^oK	T^oR	$\log p_C/a_C$	p^o_C	$\log p_{C_2}/a^2_C$	$p^o_{C_2}$	$\log p_{C_3}/a^3_C$	$p^o_{C_3}$	$\log p_{C_4}/a^4_C$	$p^o_{C_4}$	$\log p_{C_5}/a^5_C$	p_{C_5}
3500	6300	-2.50	0.0031	-2.50	0.0031	-1.95	0.011	-3.76	0.0002	-3.60	0.0003
3600	6480	-2.20	0.0063	-2.16	0.0069	-1.63	0.023	-3.37	0.0004	-3.20	0.0006
3700	6660	-1.93	0.012	-1.84	0.0145	-1.33	0.047	-2.99	0.001	-2.82	0.0015
3800	6840	-1.66	0.022	-1.54	0.029	-1.06	0.087	-2.63	0.0024	-2.45	0.0036
3900	7020	-1.41	0.039	-1.26	0.055	-0.79	0.16	-2.28	0.0055	-2.11	0.0078
4000	7200	-1.18	0.066	-0.99	0.102	-0.54	0.29	-1.96	0.011	-1.79	0.016
4100	7380	-0.96	0.11	-0.73	0.19	-0.30	0.50	-1.65	0.022	-1.48	0.033
4200	7560	-0.74	0.18	-0.49	0.32	-0.07	0.85	-1.36	0.044	-1.19	0.065
4300	7740	-0.53	0.30	-0.25	0.56	+0.14	1.38	-1.08	0.083	-0.91	0.123
4400	7920	-0.33	0.47	-0.03	0.93	0.35	2.24	-0.81	0.155	-0.64	0.229
4444	8000	-0.25	0.56	+0.06	1.15	0.44	2.76	-0.70	0.20	-0.53	0.295
4500	8100	-0.15	0.71	+0.18	1.51	0.54	3.47	-0.56	0.28	-0.40	0.400
4600	8280	+0.03	1.07	+0.38	2.40	0.73	5.37	-0.32	0.48	-0.15	0.71
4700	8460	0.20	1.59	+0.58	3.80	0.91	8.13	-0.09	0.81	+0.08	1.20
4800	8640	0.36	2.29	+0.76	5.76	1.08	12.0	+0.13	1.35	0.30	2.00
4900	8820	0.52	3.31	0.94	8.71	1.24	17.3	+0.36	2.29	0.51	3.24
5000	9000	0.67	4.7	1.11	12.89	1.40	25.1	0.55	3.55	0.72	5.25
5100	9180	0.81	6.5	1.27	18.62	1.55	35.5	0.74	5.50	0.91	8.13
5200	9360	0.95	8.9	1.43	26.92	1.69	49.0	0.93	8.51	1.10	12.6
5300	9540	1.08	12.0	1.58	38.02	1.83	67.6	1.11	12.90	1.27	18.63
5400	9720	1.21	16.2	1.72	52.50	1.96	91.2	1.28	19.10	1.44	27.55
5500	9900	1.34	21.9	1.86	72.45	2.09	123	1.44	27.55	1.61	40.74
*5555	10,000	1.41	25.7	1.94	87.10	2.16	145	1.53	33.90	1.70	50.1
5600	10,080	1.46	28.8	2.00	100	2.21	162	1.60	39.80	1.77	58.9

* Extrapolated

TABLE 2A

PRESSURE OF CARBON POLYMORPHS OVER

Zr-C ALLOYS AT 9000° R

x	a_C	p_C	p_{C_2}	p_{C_3}	p_{C_4}	p_{C_5}	$p_C(T)$
0.01	0.0005	0.0023					0.002
0.10	0.0082	0.0384					0.038
0.20	0.0278	0.1298	0.01				0.140
0.30	0.0662	0.3096	0.06	0.01			0.380
0.40	0.1317	0.616	0.22	0.06			0.896
0.50	0.2312	1.081	0.68	0.31	0.01		2.08
0.60	0.3662	1.713	1.73	1.23	0.06	.03	4.76
0.70	0.5303	2.480	3.62	3.74	0.28	.21	10.33
0.80	0.7071	3.307	6.45	8.88	0.89	.95	20.48
0.90	0.8726	4.081	9.82	16.69	2.06	2.68	35.33
0.99	0.9897	4.629	12.63	24.35	3.41	4.99	50.00

TABLE 3A

PRESSURE OF CARBON POLYMORPHS OVER

Nb-C ALLOYS AT 9000 AND 10,000 ^{o}R

a) 9000^{o} R

x	a_C	p_C	p_{C_2}	p_{C_3}	p_{C_4}	p_{C_5}	p_C (T)
0.01	0.0003	0.0012					0.001
0.10	0.0047	0.022					0.02
0.20	0.0179	0.084					0.08
0.30	0.0472	0.221	0.03				0.25
0.40	0.1028	0.481	0.14	0.03			0.65
0.50	0.1964	0.910	0.50	0.19	0.01		1.61
0.60	0.3280	1.534	1.39	0.88	0.04	0.02	3.86
0.70	0.4984	2.331	3.20	3.09	0.22	0.16	9.00
0.80	0.6880	3.218	6.10	8.14	0.79	0.81	19.06
0.90	0.8470	3.961	9.25	15.18	1.82	2.28	32.49
0.99	0.9897	4.629	12.64	24.25	3.41	4.99	48.92

b) 10,000^{o} R

x	a_C	p_C	p_{C_2}	p_{C_3}	p_{C_4}	p_{C_5}	p_C (T)
0.01	0.0004	0.009					0.01
0.10	0.0064	0.160					0.16
0.20	0.0227	0.570	0.01				0.58
0.30	0.0567	1.423	0.08	0.02			1.52
0.40	0.1177	2.954	0.36	0.14	0.01		3.46
0.50	0.2138	5.366	1.17	0.85	0.07	0.02	7.48
0.60	0.3483	8.742	3.12	3.67	0.50	0.26	16.29
0.70	0.5168	12.972	6.86	12.01	2.42	1.84	36.10
0.80	0.6984	17.530	12.53	29.70	8.07	8.32	76.15
0.90	0.8698	21.832	19.44	57.31	19.39	24.90	142.87
0.99	0.9897	24.841	25.17	84.49	32.54	47.50	241.54

NASA-Langley, 1965 E-3102